Characterization of Syncrude Sludge Pond Tailings*

Abdul Majid[1], V.J. Boyko[1], Bryan D. Sparks[1], John A. Ripmeester[1] and H. Kodama[2]

1. Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, K1A 0R9 Canada

2. Chemistry and Biology Research Institute, Ottawa Ontario, K1A 0R6 Canada

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The hot water process used by Suncor and Syncrude to extract bitumen from the Athabasca Oil Sands produces large volumes of tailings slurry. The fine grained sludge component of this waste is the most troublesome because of its stability and poor compaction potential. The sludge apparently owes its stability substantially to a complex interaction between organic coated amorphous particles, clays and bitumen. In this study we have investigated the nature of both the minerals and the associated organic matter present in a thickened, aqueous tailings sludge sample, from the Syncrude Canada Limited plant. An oil phase agglomeration technique was used to remove free bitumen and associated oil wettable solids from the sludge. On standing, the treated sludge, unlike a comparable blank, separated into settling and non-settling fractions. The solids from these fractions were analyzed by; X-ray diffractometry, Inductively Coupled Plasma Atomic Emission Spectrometry, Solid State MAS ^{29}Si and ^{27} Al NMR spectroscopy in an attempt to characterize the inorganic minerals present. The oil phase solids showed considerable enrichment in heavy metals compared to the other solids. The findings of this study could be helpful in providing some insight into the nature of tailings pond sludge, a problem which poses the most imminent environmental constraint to future use of the "hot water" process.

INTRODUCTION

Two commercial oil sand extraction plants in Alberta generate vast quantities of tailings slurry as a result of the hot water extraction of bitumen from tar sands.[1-3] The fine-grained sludge component of this waste is the most troublesome because of its stability and poor compaction potential. The reason for the intractability of the sludge has been the subject of considerable study.[1,3-7] Based on some recent studies, it is generally believed that toluene insoluble organic matter (IOM) associated with certain

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largely amorphous solids could be partly responsible for the stability and incompressibility of the oil sand slimes.[2,5-7] It is believed that the IOM causes particle surfaces to develop some hydrophobic character, allowing particle bridging, possibly through the medium of residual bitumen, thereby setting up a gel structure.[7,8] Another reason for the stability of oil sands sludge is said to be the presence of fine clay platelets which, with their differential edge and force-wetting properties, can also assist in the stabilization of suspensions[2,9].

In our previous work, we have isolated and characterized insoluble organic matter from a number of oil sand tailings streams obtained from both the Suncor and Syncrude plants.[6,7] More recently we have fractionated sludge from the main Syncrude Canada Ltd. tailings pond. After removal of the emulsified bitumen by an oil phase agglomeration technique the sludge solids separated into settling and non-settling fractions. The insoluble organic matter associated with the fines present in the non-settling portion of the sludge was concentrated by an acid dissolution scheme[6] and then characterized using elemental analysis and solid state ^{13}C NMR spectroscopy[10]. In this communication we, report the analysis of inorganic mineral fractions using X-ray diffractometry, Inductively Coupled Plasma Atomic Emission Spectrometry, and ^{29}Si and ^{27} Al NMR Spectroscopy.

EXPERIMENTAL METHODS

Sample

Aqueous sludge from the 17 m level of the Syncrude tailings pond[11,12] was provided to us by Drs. R. Schutte and L. Danielson of Syncrude Canada Ltd. in 4-litre jugs. Prior to further sub-sampling, the samples were thoroughly mixed by vigorous manual agitation.

Oil Phase Agglomeration Treatment

A countra-rotating stirring device (grease kettle) was used to remove bitumen from the sludge[10,13] using vacuum still bottoms as the oil collection phase. After removal of bitumen the aqueous sludge was fractionated as shown in Figure 1. The aqueous phase was transferred into a 500 mL beaker and the contents allowed to gravity settle for one week. The suspension was then decanted off to leave the settled solids. Water was evaporated at 100°C to obtain the solids from the supernatant liquor. The dried solids fraction from the suspension was deminieralized using HCl and HF in order to concentrate the organic matter associated with the mineral fines[6].

NMR Measurements

^{29}Si MAS NMR spectra (spinning rate ≈3.5kHz) were recorded at 59.60 MHz on a Bruker MSL-300 NMR spectrometer (magnetic field 7.1 T). About 4,000 free-induction decays (FIDs) were accumulated at a repetition time of 2s. Chemical shifts are given in ppm with respect to tetramethylsilane (TMS).

^{27}Al MAS NMR spectra were recorded at 78.172 MHz on the same instrument using a repetition time of 1s. The number of free-induction decays accumulated were 6 for solids VI and 145 for the other two samples. ^{27}Al chemical shifts were measured with respect to solid $Al(H_2O)_6^{3+}$.

Mineral Composition. Mineral (crystalline) composition of the samples was determined semi-quantitatively by comparing their X-ray diffraction (XRD) peak intensities with those of standards. XRD patterns were recorded using a SCINTAG PAD V automated powder diffractometer equipped with a graphite monochromator, using CoKα radiation (λ= 1.7902Å). The amount of each of the minerals in the samples was estimated by multiplying the peak intensity of the characteristic reflection for the respective mineral by the intensity factor for that mineral, determined from XRD data for a set of standard mixtures. The standards were measured under identical experimental conditions, including sample preparation radiation source and diffraction geometry. The amount of poorly-crystalline components (X-ray amorphous) was expressed by the difference of 100 and the total % of crystalline components.

Heavy Metal Analysis. Quantitative Industively Coupled Plasma Atomic Emission Spectroscopic methods (ICP-AES) were used to analyze the ash for Ti, Zr, Cu, Ni, Cr, Mn, Al, Ca, Fe and Mg.

RESULTS AND DISCUSSION

The separated solids fractions were treated according to the scheme shown in Figure 2. The non-settling portion was leached with HCl and HF in order to concentrate the insoluble organic matter associated with this fraction. Table I lists the semi-quantitative X-ray diffraction analysis of the mineral matter fractions shown in Figures 1 and 2. The following conclusions are obvious from examination of the data in Table I.

1. The proportion of amorphous material was higher in the suspended solids than in the sediment.

2. Solids obtained from the washing of the oil phase had the lowest quantity of amorphous material and the highest quartz content of all the solids fractions.

3. The proportion of mica and kaolinite clays in the sediment was higher than in the non-settling solids.

4. There is an unexpected discrepancy in the determination of amorphous material in the ashed and unashed samples of solids II and III.

These results suggest that removal of bitumen has a marked effect on the structure of sludge, freeing the bulk of the crystalline minerals and allowing them to freely settle out. Also, the remaining suspended solids, associated with larger amounts of amorphous material and insoluble organic carbon (IOC), were found to settle more readily, although slowly, from the treated sludge than from the untreated sludge. This suggests that bitumen present in the sludge interacts with some component of the sludge solids to form a structure which is capable of entrapping particles that would otherwise settle.

Table II lists the elemental analyses of ashed solids obtained from the fractionation of Syncrude sludge. Solids III obtained by washing the oil phase, after sludge treatment, contained the lowest concentrations of heavy metals which is consistent with the very high quartz content found in these solids. Solids IV (suspension solids) had higher concentrations of Al, Mg and Zr but lower concentrations of Cr and Mn than solids II from the sediment. Concentrations of Ti, Fe and Ca in the two fractions was similar. Whereas solids IV from the suspension comprise a large proportion of both the X-ray amorphous material and the elements Al, Mg and Zr it seems likely that these components are directly associated.

Leaching of the suspension solids IV with dilute HCl dissolved the Ca and Mn almost quantitatively plus the greater part of the Fe, Al, Mg and Cr. However, Ti and Zr appeared to resist dissolution by HCl as seen from the enrichment of these elements in the HCl extracted solids V.

Treatment of solids V by HF produced a solution with Al as the major element followed by Fe, Ti and Zr. Minor constituents in the HF solubles included Mg, Ca, Cr and Mn.

Table III lists the elemental distribution among solids fractions VI to VIII. It is obvious from this data that the bulk of the Ti and Zr has been unaffected by treatment with HCl and HF with over 60% of these elements being insoluble. Thus it seems likely that Ti and Zr are strongly complexed with the IOM and that these complexes are not readily decomposed by the acid treatment.

Almost quantitative dissolution of Ca and Mn in HCl was achieved, suggesting that these elements are not complexed to IOM but are present as inorganic minerals. Al, Fe, Mg and Cr exhibit an intermediate solubility, indicating that they could be present as a mixture of free inorganic minerals and as complexes with the IOM.

Solid State ^{29}Si and ^{27}Al MAS NMR

The ^{29}Si MAS NMR spectrum of non-settling solids from suspension (Figure 3a) shows a sharp resonance at 92 ppm from TMS with a very weak shoulder around -88 ppm. These features fall in the ^{29}Si chemical shift range of layer structured phyllosilicate (Q^3) minerals[14]. Examples of these minerals include trioctahedral silicates like serpentine and dioctahedral aluminosilicates like pyrophyllite and kaolinite.

The ^{27}Al MAS NMR spectra of dried sludge and suspension solids from clean sludge are shown in Figures 3b and 3c respectively. Both spectra consist of a single peak at -4 ppm with respect to $[Al\ (H_2O)^6]^{3+}$ as an external reference. This suggests that Al in these samples is exclusively in octahedral coordination.

On treatment of suspension solids with 6M-HCl ≈ 30% of the material leached out. Infrared and DC-Arc spectrographic analysis of this material was consistent with $AlCl_3\ xH_2O$ being the major component and Zn, Fe species as trace amounts. Figure 3d is the ^{27}Al MAS NMR spectrum of this material. The spectrum consists of a single sharp peak at -1 ppm indicating the presence of octahedral Al alone.

CONCLUSIONS

1. The suspension solids separated after oil phase agglomeration of Syncrude sludge contained a higher proportion of X-ray amorphous material than the settled solids. The suspension solids also had a higher concentration of Al, Mg and Zr suggesting that these elements were associated with the amorphous solids.

2. The resistance of Ti and Zr towards dissolution by HCl and HF suggests that these metals could be complexed with insolube organic matter (IOM).

3. Al, Fe and Cr appear to be present as a mixture of soluble inorganic minerals and as insoluble complexes with IOM.

4. Solid state ^{29}Si NMR spectrum of the suspension solids suggested the presence of phyllosilicate minerals, conforming to the minor amounts of kaolinite detected by X-ray diffractometry.

5. Solid state ^{27}Al NMR spectra indicated that Al in these samples was exclusively in the octahedral coordination.

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Table I Semi-quantitative X-ray Diffraction Analysis of Mineral Matter Fractions from Syncrude Sludge Pond Tailings*

Fraction No.†	Description	Concentration Range (wt. %) Mica	Kaolinite	Quartz	X-ray Amorphous
–	Dried Untreated Sludge				
	Un-ashed	10-25	10-25	10-25	40
	Ashed	10-25	10-25	10-25	40
1	Sediment from Untreated Sludge				
	Un-ashed	10-25	10-25	25-40	25-40
2	Sediment from Clean Sludge				
	Un-ashed	10-25	10-25	25-40	25-40
	Ashed	10-25	25-40	25-40	1-10
3	Washings from Recovered Bitumen				
	Un-ashed	1-10	1-10	40	10-25
	Ashed	10-25	1-10	40	1-10
4	Suspension Solids from Clean Sludge				
	Un-ashed	1-10	1-10	1-10	>40
	Ashed	1-10	1-10	1-10	>40
5	HCl Treated Suspension Solids from Clean Sludge				
	Un-ashed	1-10	1-10	1-10	>40
	Ashed	1-10	1-10	1-10	>40

* In addition to the amount of major minerals listed in the table, small amounts of the following minerals were also detected in some of these fractions:
Interstratified Minerals minor amounts (1~10%) in Fractions 1,2 and dried sludge;
Microcline , trace (<1%) in Fraction 1; Plagioclase, trace (<1%) in dried sludge;
Lepidocrocite minor quantities in dried sludge, and Siderite in minor quanitites in Fraction 2

† According to Figure 1 and 2

Table II The Elemental Composition of the Mineral Portion of Various Fractions from Syncrude Sludge Pond Tailings (Figures 1 and 2)

Fraction No.†	Yield (g/100 g sludge)	Ash (wt %)	C (wt%)	Elemental Analysis (wt. % of ash)*							
				Ti	Fe	Al	Ca	Mg	Zr‡	Cr‡	Mn‡
1	2.0	94.2	3.7	0.5	2.2	8.8	0.18	0.41	180	88	620
2	11.5	94.3	3.7	0.56	2.9	10.3	0.25	0.41	130	220	950
3	1.6	83.3	3.0	0.40	0.5	3.5	0.02	0.12	100	33	52
4	13.0	92.4	5.8	0.50	2.4	12.5	0.25	0.72	230	120	410
5	9.0	88.9	7.9	0.73	1.4	7.3	0.011	0.22	330	67	21
6	2.2	100**	1.9	2.05	3.6	16.3	0.06	0.1	930	190	53
OPS	0.1	70	17.3	1.7	10.5	7.4	N.D.	N.D.	660	7200	N.D.

† Figures 1 and 2
‡ as ppm
N.D. not determined
* Cu and Ni in all fractions other than OPS were below the detection limit of the instrument. Concentration in OPS: Ni - 0.23%; Cu - 490 ppm; V - 190 ppm
** Analyzed as un-ashed samples

Table III Elemental Distribution by Repeated Acid Leaching of Non-settling Solids from Syncrude Sludge

Fraction	Elemental Distribution (wt. % of amount in solids IV)*							
	Ti	Fe	Al	Ca	Mg	Zr	Cr	Mn
Solids VI; HCl Solubles	2.8	61.1	61.1	97.1	79.6	4.4	62.8	96.6
Solids VIII, HF Solubles	75.10	27.5	23.9	4.4	2.5	74.1	29.0	2.4
Solids VII**	22.1	11.5	15	-	17.9	21.5	8.2	1.0

* HCl Solubles = $\frac{y-x}{y} \times 100$ where y = Elemental amounts in solids IV calculated as:
Elemental concentrations from Table II x 0.13 (yield fraction) x 0.924 (ash fraction)

X = Elemental amounts in solid V calculated as:
Elemental concentrations from Table II x 0.09 (yield fraction) x 0.889 (ash fraction)

HF Solubles = $\frac{z}{y} \times 100$ where z = Elemental considerations from Table II x 0.022 (yield fraction)

** calculated by difference

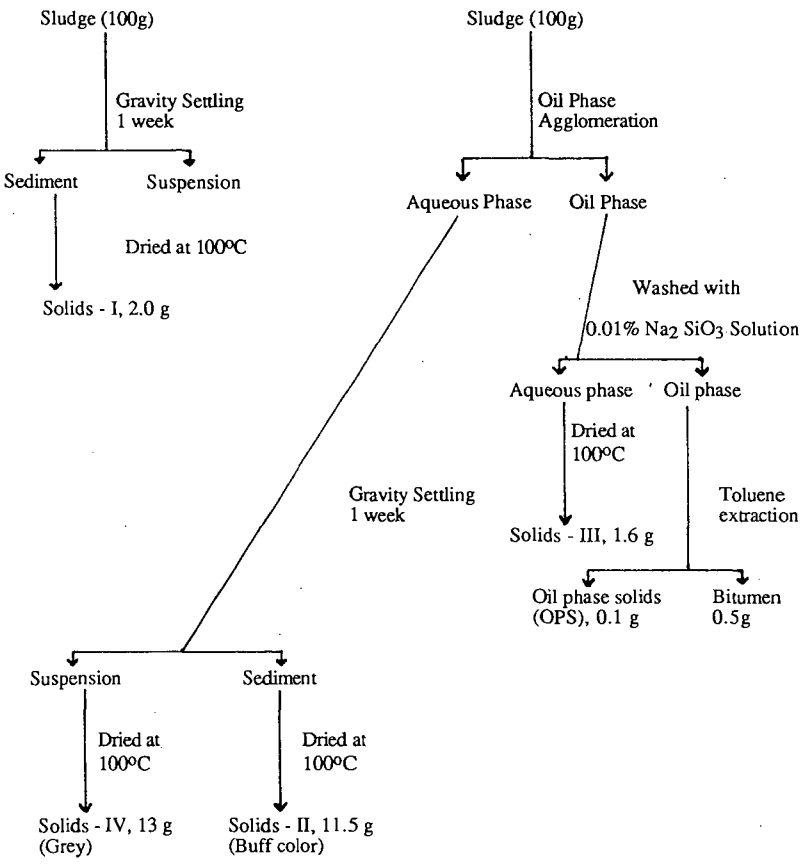

Figure 1. Fractionation scheme for Syncrude Sludge Pond Tailings.

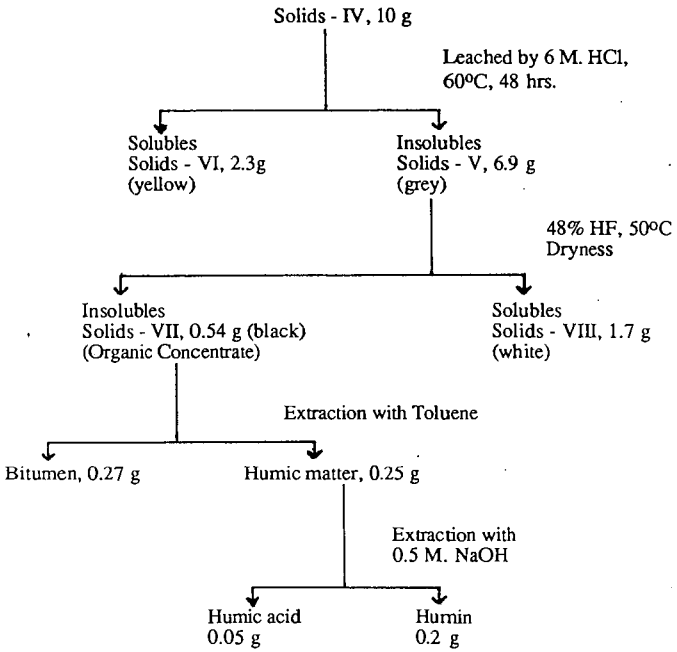

Figure 2. Flow sheet for the treatment of non-settling solids by successive acid leaching and extraction of humic acids

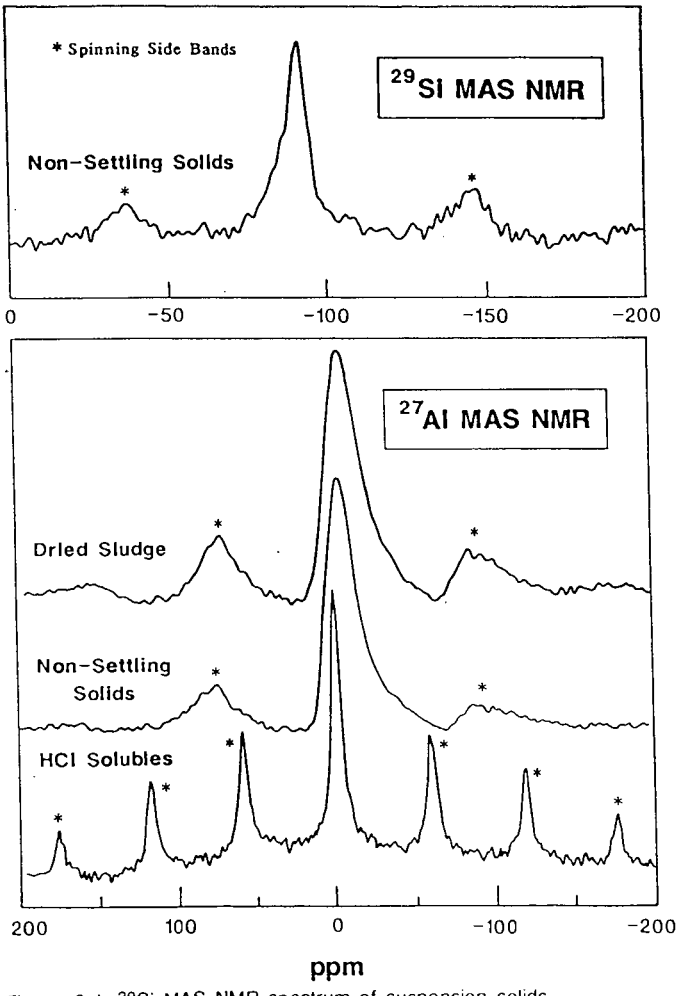

Figure 3a) ^{29}Si MAS NMR spectrum of suspension solids.

b-d) ^{27}Al MAS NMR spectra of b) dried Syncrude Sludge, c) suspension solids from clean sludge and d) HCl solubles from suspension solids.